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1

LUMINESCENT COMPOSITIONS

The present invention relates to luminescent organic compositions which are capable of emitting circularly polarised light and also to light emitting devices incorporating such compositions. Examples of such devices contemplated by the invention include Organic Light Emitting Diodes (OLEDs) e.g. as light sources for "backlighting" Liquid Crystal Displays (LCDs) or as display devices in their own right.

Modern consumer electronics require cheap, light contrast displays with good power efficiency and low drive voltages. This is increasingly important with the development of mobile communications.

Currently flat panel displays are provided predominantly by LCDs, e.g. Twisted Nematic LCDs (TN-LCDs) with active matrix addressing and Super-Twisted Nematic LCDs (STN-LCDs) with multiplex addressing. There is however a disadvantage with LCDs in that they are of low intrinsic brightness and intense back lighting is required which in turn is a heavy drain on power. This low intrinsic brightness is due to high losses of light caused by the absorbing polarisers and filters which result in external transmission efficiencies of around 1% [1]. These losses can be reduced by providing a back light source which itself emits polarised light of a high polarisation ratio, in excess of 100:1 (although lower values (in excess of 10:1) can be employed if a "clean-up" polariser is also used). The use of such a light source avoids the need for one of the polarisers in the LED thus improving brightness. The light source may be a electroluminescent (EL) light source and the combination of organic EL and LCD technologies offers the possibility of low cost, bright portable displays with the combined benefits of simplified manufacturing and enhanced power efficiency. Thus, the development of OLEDs [2-4] offers the prospect of a light source with polarised electroluminescence for LCDs with a lower power consumption and high brightness.

2

[3] OLEDs also represent the main competitor to Liquid Crystal Displays (LCDs) in the flat panel displays market as well as being a potential source of polarised emission for LCDs.

OLEDs are characterised by low operating voltages and power consumption, wide viewing angles and high brightness and contrast ratios. Thus, they are compatible with portable applications. High-information-content OLEDs using organic materials can be addressed using direct addressing, multiplex addressing or active matrix addressing.

OLEDs are currently fabricated using electroluminescent low-molar-mass materials or aromatic conjugated electroluminescent polymers with a high glass transition temperature (T_g). Both of these classes of organic materials require a high T_g value in order to avoid crystallisation, which can degrade device performance severely. Indeed, life-time has been the major obstacle to commercialisation of this otherwise attractive technology. However, commercial OLEDs using low-molecular weight materials and polymer are starting to appear on the flat-panel displays market in significant volumes. Typically EL polarisation ratios of 30 to 40 for linearly (plane) polarised light are desired, but with the use of a clean up polariser EL ratios of 10 or more are adequate. However, circularly polarised light can also be converted into a source of linearly polarised light by the very efficient transformation of the emitted circularly polarised light into plane polarised light by the use of an inexpensive quarter-wave ($\lambda/4$) plate with very little loss.

Plane polarised EL can be achieved from uniaxially aligned chromophores with best results obtained from polymers to date. [3,4] An EL polarisation ratio of 12:1 with 200 cd m^{-2} was found from *para*-phenylene vinylene rubbed at high temperatures when partially-formed from its soluble polymer precursor. [5] A better ratio of 15:1 but with lower brightness was reported for liquid crystalline polyfluorene films oriented using rubbed polyimide. [6] However, in addition to problems associated with mechanical rubbing, these high molecular weight polymers can possess

disadvantages such as high viscosity, leading to long annealing times at high temperatures. The macroscopic alignment of the chromophore for polarised EL has been achieved by a variety of methods including mechanical stretching [7,8], rubbing [9] and Langmuir-Blodgett (LB) deposition [10]. Very large polarisation ratios for photoluminescence have been obtained from stretch-oriented films of MEH-PPV, i.e. poly(2-methoxy-5-[2'-ethyl-hexyloxy]-*para*-phenylene vinylene. [11] However, implementation in active EL configurations proves problematic for films of thickness ≤ 1 µm due to degradation of the structural integrity of the film at the high draw ratios required. In contrast, LB deposition creates macroscopically oriented thin films of a few nm thickness. Unfortunately, the LB deposition technique is not compatible with large-scale production of commercial devices. Crystallisation of LB films over time is also a major problem.

Because of these factors, rubbed polyimide [5,6,12] has remained until now the most attractive process for aligning luminescent chromophores, especially in the liquid crystalline state, for potential commercial applications. Even so, the rubbing process does have several potential drawbacks as it can cause mechanical damage and generate electrostatic charge. Hence leakage currents result, which can significantly reduce device lifetimes.

The conversion of macroscopically oriented reactive mesogens (liquid crystals) to an intractable network provides an alternative route to polarised EL. This technique involves the polymerisation and crosslinking of reactive liquid crystal monomers *via* photo-polymerisable and/or thermally polymerisable end-groups of the molecule. Low temperature processing is possible and multilayer devices can be constructed with carrier-transporting layers deposited on top of the insoluble crosslinked network. Sub-pixellation can also be achieved by selective photopatterning. Polarised EL with a dichroic ratio of 2 was achieved only by doping a liquid crystal network with a photoactive perylene dye. [13] Other authors quote polarised absorbance and PL. [14,15] EL was not reported. We have recently demonstrated for the first time that efficient emission of linearly polarised light is

4

possible using this approach. [16-18] Electroluminescence with a polarisation ratio of 11:1 from a uniformly aligned nematic network was achieved. Diene photo-active end-groups were used, which polymerise by a selective cyclisation reaction. Surface alignment was achieved using a doped polymer photoalignment layer, oriented by exposure to a polarised UV light. Threshold voltages between 2 V and 8 V were found and a maximum brightness of 400 cd m^{-2} was obtained. This combination of photo-crosslinking and non-contact alignment technology shows that polarised, patterned, multilayer organic electroluminescent displays can be made using standard photolithography techniques at room temperature.

The use of circularly polarised light as a light source is much less advanced, although potentially of equal or greater value. Circularly polarised light has been generated by photoluminescence and electroluminescence using three main methods [3] involving macroscopically aligned chiral nematic liquid crystals;

a) a guest-host system involving a photoluminescent guest molecule in a chiral nematic host [19];

b) mainchain conjugated polymers with optically active (chiral) pendent chains [20,21]; and

c) chiral nematic glasses [22-24].

The chiral nematic phase (N*) is the helical equivalent, induced by the presence of at least one optically active material, of the usual nematic state. This results in a macroscopic helical structure in which the director rotates through 360° over the pitch length of the chiral nematic phase. The optical properties of the chiral nematic phase originate from this twisted structure, e.g., high optical rotation of plane polarised light under certain conditions, circular dichroism and the selective (Bragg) reflection of circularly polarised light in a narrow band of wavelengths related to the pitch of the helix.

An unusual feature of a chiral nematic helix is that one hand of circularly polarised light is reflected and one hand is transmitted. The central wavelength of selective reflection is given by

$$\lambda_s = p.n \qquad (1)$$

where p is the pitch of the chiral nematic helix and n is the average refractive index ($n_o + n_e/2$). The pitch of a chiral nematic phase is temperature dependent since both refractive indices of a liquid crystal vary with temperature. The bandwidth of selective reflection is given by

$$\Delta\lambda = \lambda_s n/\Delta n \qquad (2)$$

where Δn is the birefringence ($n_o - n_e$) of the chiral nematic liquid crystalline phase.

The highest degree of circular polarisation of emitted light obtained from a luminescent chiral nematic system has been achieved by matching the wavelength of emission to the wavelength of selective reflection of the chiral nematic helix in the so-called resonance region. The degree of circular polarisation can be defined by the dissymmetry factor g_e

$$g_e = 2(I_L - I_R)/(I_L + I_R) \qquad (3)$$

where I_R and I_L are the intensity of right-handed and left-handed, respectively, of the emitted circularly polarised light, or by the ratio of I_R to I_L (or the inverse). These parameters are clearly related and should be as high as possible for practical applications. The magnitude of g_e varies from 0 for unpolarised light to ±2 for completely circularly polarised light. Values of -1.5 to +0.8 were achieved in the resonance region using chiral nematic liquid crystals stabilised in the glassy state.

6

However, an inversion in sign in the resonance region was observed inexplicably. The g_e factor also changed significantly with wavelength and the wavelength integrated value of g_e is low. Furthermore, such high values were only achieved using very thick cells, e.g., 35 μm. Unfortunately chiral nematic conjugated polymers exhibit very low g_e values, e.g., 5×10^{-3}.

It is an object of the present invention to obviate or mitigate at least some of the abovementioned disadvantages.

According to a first aspect of the present invention there is provided a composition capable of emitting circularly polarised light comprising a medium including a chiral, helical liquid crystalline phase with a substantially fixed, temperature independent helical pitch, said liquid crystalline phase being comprised of calamatic liquid crystal molecules having a luminescent moiety and the composition being such that excitation of the luminescent moiety causes the medium to emit light in the bandwidth of selective reflection of the liquid crystalline phase.

According to a second aspect of the present invention there is provided a light emitting device comprised of a cell having a pair of opposed sides and containing a composition as defined for the first aspect of the invention, at least one of said sides being transparent to the polarised light emitted by said composition on excitation of the luminescent moiety.

Light emitting devices in accordance with the second aspect of the invention may be produced by providing a cell having a pair of opposed walls at least one of which is provided on its interior surface with an alignment layer and filling the cell with a formulation (which is a precursor to the composition of the invention) which incorporates calamatic liquid crystal molecules having a luminescent moiety and which is capable of being assembled by said alignment layer(s) to a chiral, helical liquid crystalline phase, assembling said formulation into said liquid crystalline phase, and immobilising said phase so as to provide the latter with a substantially fixed,

temperature independent helical pitch. As described more fully below, the immobilisation (to produce the composition of the invention) may be effected by converting the precursor formulation into a glass by quenching that composition to below its glass transition temperature (T_g). Alternatively the calamatic liquid crystal molecules may incorporate polymerisable moieties (e.g. olefinic double bonds) such that the composition may be polymerised to form a network in which the helical liquid crystalline phase has a fixed, temperature independent pitch.

According to a third aspect of the present invention there is provided a medium including a chiral, helical liquid crystalline phase in the form of a glass, said liquid crystalline phase being comprised of calamatic liquid crystal molecules having a luminescent moiety and the composition being such that excitation of the luminescent moiety causes the medium to emit light in the bandwidth of selective reflection of the liquid crystalline phase.

According to a fourth aspect of the present invention there is provided a medium including a chiral, helical liquid crystalline phase in the form of a polymerised network, said liquid crystalline phase being comprised of calamatic liquid crystal molecules having a luminescent moiety and the composition being such that excitation of the luminescent moiety causes the medium to emit light in the bandwidth of selective reflection of the liquid crystalline phase.

The compositions of the invention (which as indicated may be glasses or polymer networks) are comprised of calamatic liquid crystal molecules which incorporate a luminescent moiety and which are 'assembled' in a chiral, helical liquid crystalline phase. The preferred range for the "length" of the helical pitch of the composition is 0.2 μm to 0.5 μm. In use the luminescent moiety is activated (in ways described more fully below) to generate light which is within, or is converted to be within, the bandwidth of selective reflection of the helical liquid crystalline phase. As a result, and due to the abovedescribed properties of a chiral, helical liquid crystalline phase, circularly polarised light is emitted.

8

By ensuring that the liquid crystalline phase has a substantially constant, temperature independent helical pitch, the 'stopband' (i.e. the bandwidth of selective reflection) is temperature independent so that the luminescent properties are likewise independent of temperature.

The use of the calamatic liquid crystal molecules is an important feature of the invention since it is these molecules which allow light emitting devices which are much thinner than those achieved using the "disk-like" molecules in the chiral nematic glasses, [22-24]. Calamatic liquid crystal molecules as employed in this invention exhibit high refractive indices and a large birefringence. This allows the use of thin cells, which is especially advantageous for electroluminescence where the switch-on and operating voltages increase with cell thickness. Furthermore, calamatic liquid crystal molecules as employed in this invention posses a relatively low value for the flow viscosity, which allows them to be oriented efficiently with a high order parameter on alignment layers, especially photoalignment layers. This contributes to the high values of the polarisation ratios of circularly polarised light obtained using cells incorporating these calamitic liquid crystals. A further advantage of the calamatic liquid crystal molecules as employed in this invention is the ability to so modify their chemical structure to obtain high charge mobility, especially of holes, through them. This is advantageous for the construction of efficient OLEDs containing them as described below.

The compositions exhibit an intrinsic high value of birefringence (Δn) which results in high reflectivity in the light emitting devices and a broad bandwidth of selective reflection (see equation 2 above). Circularly polarised electroluminescence with high I_L to I_R ratios (>15:1) can be predicted from devices with a thickness, $d >> \lambda_s/n$, so a high value of the average refraction index, n, enables thin devices to be made for light of a given wavelength, e.g. in the visible spectrum. The rod-like or lathe-like nature of calamatic liquid crystal molecules as employed in this invention with their high length-to-breadth ratio and highly conjugated and rigid aromatic

9

molecular cores automatically gives rise to high values for the refractive indices and the birefringence. The value of d (i.e. the width of the "gap" in the cell) may for example be in the range of 1 to 10 microns. Thinner devices could be used to provide lower, but acceptable, $I_L:I_R$ ratios.

The chiral, liquid crystalline phase of the composition of the invention is preferably a chiral nematic phase but may also be a chiral smectic C phase. The chirality of the phase may be by virtue of the calamitic liquid crystalline molecules having at least one chiral centre. Alternatively these molecules may be achiral and a chiral dopant is provided in the liquid crystalline phase. Examples of chiral dopants are disclosed in Liquid Crystals, 11, 761, 1992 and references therein.

For all embodiments of the composition in accordance with the invention, the pitch of the helical liquid crystalline phase can be "engineered" such that the bandwidth of selective reflection has the value required for the particular application of the composition. It is also possible to adjust the pitch such that the emission region exhibits rotary power or mauguin wave-guiding upon excitation of laser. The pitch can also be modulated by mixing the achiral and chiral versions of the luminescent liquid crystal molecules as employed in this invention so that the luminescence characteristics remain the same, so as not to affect energy transfer to a dye.

The luminescent moiety in the calamatic liquid crystal molecules may be photoluminescent or electroluminescent and may thus be excited accordingly to emit light which is, or is converted in the medium containing the helical liquid crystalline phase to be, within the bandwidth of selective reflection.
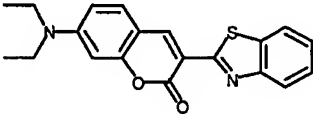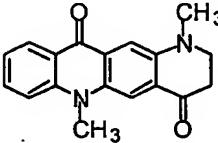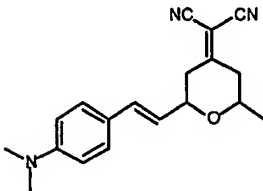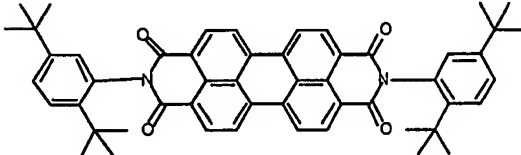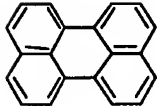
Compositions in accordance with the invention may take a number of forms.

In one embodiment of the composition, the luminescent moiety (be it photoluminescent to electroluminescent) is capable on excitation (by light or

10

application of a potential difference as appropriate) of emitting light in the bandwidth of selective reflection of the liquid crystalline phase.

In a further embodiment of the invention, the luminescent moiety (be it photoluminescent to electroluminescent) does not emit in the bandwidth of selective reflection but the composition contains a dye capable of absorbing the emission of the luminescent moiety and re-emitting light having a wavelength in the bandwidth of selective reflection.   This approach enables the fabrication of full-colour, high information-content OLEDs by pixellation of the three primary colours using luminescent dyes. Alternatively the dye can be excited by nonradiative Forster-Dexter energy transfer from a blue-emitting chiral liquid crystalline polymer network to red-emitting and green-emitting dyes.   In each case, the pitch of the helix is preferably adjusted for maximum value of the circular extinction ratio for each colour. Examples of dyes that may be used for converting blue light to red or green light are shown in the following Table 1.

11

Table 1

Molecular Structure	Acronym	colour
	Coumarin 6	red
	DMQA	green
	DCM-1	red
	TBPD	red
	perylene	orange

In the case where the luminescent moiety in the calamatic liquid crystal is photoluminescent it may be activated either by an external light source or by light from a luminescent dye provided in the medium. For the former case, the compositions of the invention are ideal for conversion of an unpolarised light source into circularly polarised light of different wavelength. Electrically pumped laser action is also possible because of the high feedback. Excitation can also be provided by current injection to provide electroluminescence from the host, which is transferred to the guest dye, which in turn emits light at a longer wavelength.

It will be appreciated from the foregoing description that compositions in accordance with the invention may readily be formulated to emit light of a predetermined wavelength. More particularly, the emission spectrum of the compositions can be easily tuned to the band width of selective reflection from the chiral helix by chemical modification and/or by blending with non-optically active analogues.

The chiral, helical liquid crystalline phase with a fixed, temperature independent helical pitch, is most preferably a Nematic phase but could also be a Smectic C phase. It is possible substantially to fix the helical pitch of the liquid crystalline phase (so that the pitch is substantially temperature independent) in a number of ways. For example, the liquid crystalline phase may be in the form of a glass in which the calamatic liquid crystals are effectively immobilised. For this purpose it is preferred that the composition of the invention has a glass transition temperature (Tg) of more than 50°C. Alternatively, the calamatic liquid crystal molecules may incorporate groups (e.g. olefinically unsaturated groups) that may be polymerised to form a network which effectively immobilises the molecules.

The calamatic liquid crystal molecules employed in the composition of the invention will generally incorporate a luminescent (photoluminescent or electroluminescent) moiety which will provide the "core" of the molecule and to which are attached two aliphatic spacer groups. The core may be a rigid, highly conjugated aromatic system. This luminescent core will usually be comprised of a number, preferably 4 to 6, conjugated aromatic rings and may comprise a fluorene "centre" each benzene ring of which is conjugated to a system of at least one (and preferably two) further aromatic ring(s), to which systems are bonded the spacer groups. Each such system may comprise a thiophene ring bonded firstly to an aromatic ring of the fluorine residue and, secondly, to a further benzene nucleus to which is bonded the spacer group.

13

Such molecules generally absorb in visible or near-UV part of the electromagnetic spectrum and emit in the visible or near infrared part of the spectrum.

Examples of suitable liquid crystal molecules are of the following formula:
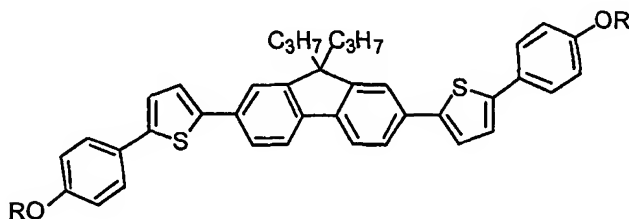
in the above formula, the R groups (which may be the same or different) represent spacer groups. Groups other than the propyl (C_3H_7-) may also be employed, e.g. alkyl groups of one, two or four carbon atoms.
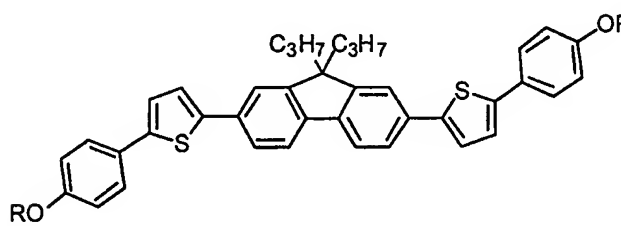
The aliphatic spacer groups preferably each contain four to sixteen carbon atoms, more preferably a chain of four to twelve carbon atoms. Preferably at least one, and preferably both, of the spacer groups has at least one branch (preferably a methyl group) which provides a chiral centre. Preferably the two spacer groups are identical with each other.
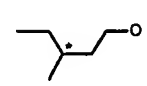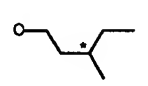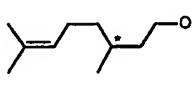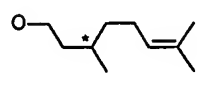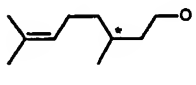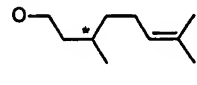
The position of the optically active centre and the nature of the branch are chosen in order to induce a chiral helical (preferably nematic) pitch in the region of the emission spectrum for optimum efficiency of generation of circularly polarised light. The closer the position of the branching group in the aliphatic spacer group is to the molecular core the smaller is the pitch. Small branching groups, such as methyl, cyano or halogen, especially fluorine and chlorine, are preferred, since they induce the desired magnitude of the pitch, contribute to the formation of liquid crystalline glasses and do not excessively depress the liquid crystalline character of the compounds incorporating them .

14

A polymerisable group may be present at the end of the spacer group. This polymerisable group may be an acrylate, methacrylate, conjugated or non-conjugated diene, a vinyl ether or an oxetane. A photopolymerisable group is preferred. It is also particularly preferred that the end groups polymerise to incorporate a cyclic structure in the polymer backbone. A non-conjugated diene, such a 1,4-pentadien-3-yl, 1,5-hexadien-3-yl or 1,6-heptadien-4-yl group, is preferred at the "end" of a spacer group. These materials can be used as thin photoluminescent or electroluminescent films as chiral nematic glasses or as crosslinked polymer networks.

The following Table 2 gives examples of calamatic liquid crystal molecules that may be employed in the invention.

Table 2. Transition temperatures (°C) for the fluorenes (1-3), where Cr-N* and Cr-I = the melting point, N*-I = the clearing point from the chiral nematic (N*) phase and t_g is the glass transition temperature.

|	RO	OR	t_g		Cr		N*	
1			(S)	•	45	•	194	(• | 173)
2			(R)	•	29	•	123	(• | 122)
3			(S)	•	23	•	123	(• | 122)

( ) Represents a monotropic transition temperature

15

Such kinds of calamatic liquid crystal molecules are especially useful for forming chiral nematic glasses.

An example of a liquid crystal molecule that may be used in the formation of polymerised network is of the above general formula (shown in Table 2) in which the R groups are of the formula:

$$-(CH_2)_x-C(O)O-R'$$
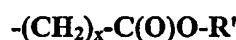
where x is 4 to 12 (preferably 4-6, e.g. 5) and R' is a 1,4-pentadien-3-yl, 1,5-hexadien-3-yl or 1,6-heptadien-4-yl group.

Devices in accordance with the second aspect of the invention may, as indicated above, be prepared by filling cells having a pair of opposed substrates at least one of which is provided on its interior surface with an alignment layer with a composition that is capable of being assembled by the alignment layer(s) into a chital helical liquid crystalline phase, and then treating the composition to fix the pitch length of the helix at a constant value.

The or each alignment layer is preferably a photoalignment layer, generated by the action of actinic light, preferably polarised ultra violet light, on a photoreactive polymer, especially such as formed by a 2+2 cyclisation reaction, as described in Chem Mater, 13, 694, 2001 and J. Phys D. Appl. Phys., 33 R67, 2000. Such layers facilitate polarised emission due to the weak wall effects on the adjacent liquid crystal medium of the photoalignment layers.

The compositions of the invention are ideal for the conversion of unpolarised light into circularly polarised light of different wavelength. If desired, the circularly polarised light can be converted to plane polarised light by a $\lambda/4$ wave plate. Electrically pumped laser action is also possible because of the high feedback.

Compositions in accordance with the invention are also highly efficient hole-transport materials which aids charge injection for efficient electroluminescence.

The compositions of the invention may be used for generating an efficient source of circularly polarised light for a number of applications, e.g. especially bright OLEDs for back lighting LCDs, lasers; notch filters etc.

The device may, for example, be photoluminescent and may be provided between a light source and a LCD as a backlight for the latter (since the device efficiently converts unpolarised light into highly circularly polarised light). Thus, the LCD would still be brighter in spite of the added presence of the photoluminescent cell between the light source and the LCD (instead of an absorbing polariser)./

Alternatively, the device may be electroluminescent device, for which purpose it may be provided with appropriate electrodes (e.g. Indium/Tin oxide). Such a device could be used as a backlight for an LCD or as a display device in its own right. Additionally there are many physical effects and photonic devices, such as optical storage devices, which would benefit from a source of highly circularly polarised light.

The invention will now be described, by way of example only, with reference to the following non-limiting Examples.

Example 1

Preparation of (S)-2,7-bis{5-[4-(3,7-dimethyloct-6-enyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene.

A mixture of 2,7-bis[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene (1.0 g, 1.7×10^{-3} mol), (S)-(+)-citronellyl bromide (1.0 g, 4.6×10^{-3} mol), and potassium carbonate (0.5 g, 3.6×10^{-3} mol) in acetonitrile (10 cm^3) was heated under reflux for

17

24 h. Excess potassium carbonate was filtered off and precipitated product rinsed through with warm acetonitrile (2 × 10 cm^3). The solution was concentrated onto silica gel for purification by column chromatography [silica gel, hexane:dichloromethane 3:1 eluting to hexane:dichloromethane 1:1] followed by recrystallisation from ethanol:dichloromethane to yield 0.58 g of (S)-2,7-*bis*{5-[4-(3,7-dimethyloct-6-enyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene, Tg, 23 °C; Cr-I, 123 °C; (N*-I, 122 °C). The PL and EL emission is yellow-green.

(The 2,7-*bis*[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene required as a starting materials was prepared described in Appendix 1).

The following compounds could be obtained analogously:

(R)-2,7-*bis*{5-[4-(3,7-Dimethyloct-6-enyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene, Tg, 29 °C; Cr-I, 123 °C; (N*-I, 122 °C).

(S)-2,7-*bis*{5-[4-(3-Methylpentyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene, Tg, 45 °C; Cr-I, 194 °C; (N*-I, 173 °C).

Example 2

Preparation   of   2,7-*bis*(2-{4-[(S)-3,7-dimethyloct-6-enyloxy]phenyl}pyrimidine-5-yl)-9,9-dipropylfluorene.

A mixture of *tetrakis*(triphenylphosphine)palladium(0) (0.06 g, 1.0 × 10^{-5} mol), 2,7-dibromo-9,9-dipropylfluorene (1 g, 2.45 × 10^{-3} mol), 2-{4-[(S)-3,7-dimethyloct-6-enyloxy]phenyl}pyrimidine boronic acid (2.16 g, 6.12 × 10^{-3} mol), 20% sodium carbonate solution (25 cm^3) and 1,2-dimethoxyethane (85 cm^3). The reaction mixture was heated under reflux overnight. The cooled reaction mixture was extracted with dichloromethane (2 × 100 cm^3) and the combined organic layers were washed with brine (2 × 50 cm^3) and dried (MgSO$_4$). After filtration the solvent was removed

18

under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane as the eluent followed by recrystallisation from dichloromethane/ethanol, to yield 1.23 g (58 %) of 2,7-*bis*(2-{4-[(*S*)-3,7-dimethyloct-6-enyloxy]phenyl}pyrimidine-5-yl)-9,9-dipropylfluorene, Tg, 24 °C; Cr-I, 113 °C; N*-I, 120 °C. The PL and EL emission is blue.

The 2-{4-[(*S*)-3,7-dimethyloct-6-enyloxy]phenyl}pyrimidine boronic acid required as a starting material was prepared as described in Appendix 1.

Example 3

Preparation of 2,7-*bis*(5-{5-[(*S*)-3,7-dimethyloct-6-enyl]thien-2-yl} thien-2-yl)-9,9-dipropylfluorene.

A mixture of 5-tributylestannyl-2-[(*S*)-3,7-dimethyloct-6-enyl]thiophene (2.23 g, 4.3 x 10^{-3} mol), 2,7-*bis*(5-bromothien-2-yl)-9,9-dipropylfluorene (1 g, 1.75 x 10^{-3} mol) and *tetrakis*(triphenylphosphine)-palladium (0) (0.2 g, 1.7 × 10^{-4} mol) in DMF (30 cm³) was heated at 90°C for 24 h. Dichloromethane (150 cm³) was added and the solution washed with 20% hydrochloric acid (2 x 150 cm³), water (100 cm³), dried (MgSO₄) and concentrated onto silica gel for purification by column chromatography [silica gel, dichloromethane: hexane 1:4] to yield 1.05 g (70 %) of 2,7-*bis*(5-{5-[(*S*)-3,7-dimethyloct-6-enyl]thien-2-yl} thien-2-yl)-9,9-dipropylfluorene, Tg, 23 °C; Cr-I, 123 °C; (N*-I, 122 °C). The PL and EL emission is yellow-green.

The 5-tributylestannyl-2-[(*S*)-3,7-dimethyloct-6-enyl]thiophene required as a starting material was prepared as described in Appendix 1.

19

Example 4

Preparation of 4,7-*bis*(5-{4-[(*S*)-3,7-dimethyloct-6-enyloxy]phenyl}thien-2-yl)-2,1,3-benzothiadiazole

A mixture of *tetrakis*(triphenylphosphine)palladium(0) (0.12 g, 1.1×10^{-4} mol), 4,7-*bis*(5-bromothien-2-yl)-2,1,3-benzothiadiazole (*1* g, 2.18×10^{-3} mol), 4-[(*S*)-3,7-dimethyloct-6-enyloxy] phenyl boronic acid (1.5 g, 5.45×10^{-3} mol), 20% aqueous sodium carbonate solution (25 cm^3) and 1,2-dimethoxyethane (90 cm^3) was heated under reflux overnight. The cooled reaction mixture was extracted with dichloromethane (2 x 100 cm^3). The combined organic layers were washed with brine (2 x 50 cm^3), dried (MgSO$_4$), filtered and evaporated down under reduced pressure. The crude product was purified by column chromatography [silica gel, dichloromethane: hexane 1:4] followed by recrystallisation from dichloromethane/ethanol to yield 0.75 g (*65 %*) of 4,7-*bis*(5-{4-[(*S*)-3,7-dimethyloct-6-enyloxy]phenyl}thien-2-yl)-2,1,3-benzothiadiazole.

The 4,7-*bis*(5-bromothien-2-yl)-2,1,3-benzothiadiazole required as starting material was prepared as described in Appendix 1.

Example 5

Preparation   of   2,7-*bis*(5-{4-[(*S*)-3-methyl-5-(1-vinylallyloxycarbonyl)pentyloxy]phenyl}thien-2-yl)-9,9-dipropylfluorene.

A mixture of 2,7-*bis*[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene, 1-vinylallyl (*S*)-6-bromo-4-methylhexanoate and potassium carbonate and *N,N*-dimethylformamide was heated under reflux overnight. The cooled reaction mixture was evaporated down under reduced pressure and the crude product purified by column chromatography on silica gel using a mixture of dichloromethane/hexane (80:20) as eluent and recrystallisation from a dichloromethane/ethanol mixture to

20

yield of 2,7-*bis*(5-{4-[(*S*)-3-methyl-5-(1-inylallyloxycarbonyl)pentyloxy]phenyl}thien-2-yl)-9,9-dipropylfluorene.

The 1-vinylallyl (*S*)-6-bromo-4-methylhexanoate required as starting material was prepared as described in Appendix 1.

Example 6

Preparation of a luminescent cell comprising a chiral nematic organic glass.

An evacuated cell made of two glass substrates, each bearing an Indium/Tin Oxide (ITO) electrode and a photoalignment layer, glued together with a UV curable glue containing spacers to form a uniform cell gap of 3.45 µm was filled with (*S*)-2,7-*bis*{5-[4-(3,7-dimethyloct-6-enyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene at 120°C under an anhydrous nitrogen atmosphere. The flow direction of the chiral nematic phase was parallel to the alignment direction of the orientation layer. The filled cell was sealed with glue and then heated to a degree above the transition from the chiral nematic phase to the isotropic liquid (clearing point) and cooled it at a rate . 0.2 °C per minute until it reached 5 °C below the clearing point. It was quenched to room temperature to form a chiral nematic glass. The cell is illuminated with a beam of collimated light at 350 nm from an argon ion laser. The stopband of the chiral nematic phase of (*S*)-2,7-*bis*{5-[4-(3,7-dimethyloct-6-enyloxy)phenyl]thien-2-yl}-9,9-dipropylfluorene ranges from 458 nm to 554 nm. The addition of 2 wt% of (*R*)-1-phenyl-1,2-ethyl *bis*-4-(*trans*-4-pentylcyclohexyl)benzoate as a chiral dopant blue-shifts the stopband range by 10 nm. The circular extinction ratio at 500 nm is 170 in transmission and 16 in photoluminescence.

Example 7

Preparation of a electroluminescent cell comprising an achiral nematic glass and a chiral dopant.

A mixture of 2,7-*bis*(5-{4-[5-(1-vinyl-allyloxycarbonyl)pentyloxy] phenyl}thien-2-yl)-9,9-dipropylfluorene and (*R*)-1-phenyl-1,2-ethyl *bis*-4-(*trans*-4-pentylcyclohexyl)benzoate is processed as characterised as described in Example 6.

Example 8

Preparation of a electroluminescent cell comprising a chiral nematic organic polymer network.

A mixture of 2,7-*bis*(5-{4-[5-(1-vinylallyloxycarbonyl)pentyloxy] phenyl}thien-2-yl)-9,9-dipropylfluorene and (*R*)-1-phenyl-1,2-ethylene *bis*-4-(*trans*-4-pentylcyclohexyl)benzoate was processed as characterised as described in Example 6 using quartz substrates instead of glass substrates. The cell is exposed with rotating linearly polarized laser light of wavelength 300 nm or 325 nm. This is achieved by using a depolarised laser light source with a rotating polarizer in front of the cell. The cell is exposed from both sides to ensure efficient crosslinking throughout the sample. The cell is characterised as described in Example 6.

22

Example 9

Colour generation by energy transfer.

A cell is filled with a mixture of Coumarin 6 and an electroluminescent mesogen, such as those described in Examples 1-5, or mixture as described in Examples 6-8, as described in Example 6. The selective reflection band of the helix is tuned to match the emission spectrum of the dye. The mesogen is excited and excitation is transferred either radiatively or nonradiatively to the dye. Red circular polarised luminescence is observed from the dye.

23

APPENDIX 1

1.   **Preparation of 2,7-*bis*[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene**

(a). A $10M$ solution of n-butyllithium in hexanes (18.0 cm^3 0.18 mol) was added slowly to a solution of fluorene (30.0 g, 0.18 mol) in THF (350 cm^3) at -50°C. The solution was stirred for 1 h at -75 °C and 1-bromopropane (23.0 g, 0.19 mol) was added slowly. The solution was allowed to warm to RT and then stirred for a further 1 h. Dilute hydrochloric acid (100 cm^3, 20%) and water (100 cm^3) were added and the product extracted into diethyl ether (3 × 150 cm^3). The ethereal extracts were dried (MgSO$_4$) and concentrated to yield 37.5 g of 9-propylfluorene as an oil.

(b). A $2.5M$ solution of n-butyllithium in hexanes (29.0 cm^3, 0.073 mol) was added slowly to a solution of 9-propylfluorene (15.0 g, 0.072 mol) in tetrahydrofuran at -50°C. The solution was stirred for 1 h at -75°C, 1-bromopropane (10.0 g, 0.092 mol) was added slowly and the temperature raised to RT after completion of the addition. After 18 h, 20% hydrochloric acid (100 cm^3) and water (100 cm^3) were added and the product extracted into diethyl ether (2 x 100 cm^3). The organic extracts were dried (MgSO$_4$) and concentrated to a pale brown oil, which crystallised overnight at RT. The product was purified by recrystallisation from methanol to yield 14.5 g of 9,9-dipropylfluorene, mp 47-49°C.

(c). Bromine (10.0 g, 0.063 mol) was added to a stirred solution of 9,9-dipropylfluorene (7.0 g, 0.028 mol) in chloroform (25 cm^3) and the solution stirred for 0.5 h. Chloroform (50 cm^3) was added and the solution washed with saturated sodium metabisulphite solution (75 cm^3), water (75 cm^3), dried (MgSO$_4$) and concentrated to yield 11.3 g of 2,7-dibromo-9,9-dipropylfluorene, mp 134-137°C.

(d). A mixture of 2,7-dibromo-9,9-dipropylfluorene (6.0 g, 0.015 mol), 2-(tributylstannyl)thiophene (13.0 g, 0.035 mol) and *tetrakis*(triphenylphosphine)-palladium (0) (0.3 g, 2.6 × 10^{-4} mol) in N,N-dimethylformamide (30 cm^3) was heated

at 90°C for 24 h. Dichloromethane (200 cm^3) was added to the cooled reaction mixture, which was washed with 20% hydrochloric acid (2 x 50 cm^3), then water (100 cm^3), dried (MgSO$_4$) and concentrated onto silica gel for purification by column chromatography [silica gel, dichloromethane:hexane 1:1]. The compound was further purified by recrystallisation from dichloromethane: ethanol to yield 4.3 g of 2,7-*bis*(thien-2-yl)-9,9-dipropylfluorene, mp 165-170°C.

(e). *N*-Bromosuccinimide[1] (2.1 g, 0.012 mol) was added slowly to a stirred solution of 2,7-*bis*(thien-2-yl)-9,9-dipropylfluorene (2.3 g, 5.55 x 10^{-3} mol) in chloroform (25 cm^3) and glacial acetic acid (25 cm^3). The solution was heated under reflux for 1 h, dichloromethane (100 cm^3) added to the cooled reaction mixture, washed with water (100 cm^3), 20% hydrochloric acid (150 cm^3), saturated aqueous sodium metabisulphite solution (50 cm^3), and dried (MgSO$_4$). The solvent was removed in vacuo and the product purified by recrystallisation from an ethanol/dichloromethane mixture to yield 2.74 g of 2,7-*bis*(5-bromothien-2-yl)-9,9-dipropylfluorene, mp 160-165 °C.

(f). A mixture of 2,7-*bis*(5-bromothien-2-yl)-9,9-dipropylfluorene (2.7 g, 4.7 x 10^{-3} mol), 4-(methoxyphenyl)boronic acid (2.2 g, 0.014 mol), *tetrakis*(triphenylphosphine)palladium (0) (0.33 g, 2.9 x 10^{-4} mol), sodium carbonate (3.0 g, 0.029 mol) and water (20 cm^3) in dimethoxyethane (100 cm^3) was heated under reflux for 24 h. More 4-(methoxyphenyl)boronic acid (1.0 g, 6.5 x 10^{-3} mol) was added to the cooled reaction mixture, which was then heated under reflux for a further 24 h. *N,N*-dimethyl formamide (20 cm^3) was added and the solution heated at 110 °C for 24 h, cooled and 20% hydrochloric acid (100 cm^3) added. The cooled reaction mixture was extracted with diethyl ether (2 x 50 cm^3) and the combined organic extracts washed with water (100 cm^3), dried (MgSO$_4$), and concentrated onto silica gel to be purified by column chromatography [silica gel, dichloromethane:hexane 1:1] and recrystallisation from an ethanol-dichloromethane mixture to yield 1.9 g (63%) of

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[1] freshly purified by recrystallisation from water

25

2,7-*bis*[5-(4-methoxyphenyl)thien-2-yl]-9,9-dipropylfluorene, Cr-N, 235 °C; N-I, 265 °C.

(g). A 1M solution of boron tribromide in chloroform (9 cm^3, 9.0 mmol) was added dropwise to a stirred solution of 2,7-*bis*[5-(4-methoxyphenyl)thien-2-yl]-9,9-dipropylfluorene (1.3 g, 2.1 × 10^{-3} mol) at 0°C. The temperature was allowed to rise to RT overnight and the solution added to ice-water (200 cm^3) with vigorous stirring. The product was extracted into diethyl ether (2 × 100 cm^3), washed with a 2M aqueous sodium carbonate solution (150 cm^3), dried (MgSO$_4$) and purified by column chromatography [silica gel dichloromethane:diethyl ether:ethanol 40:4:1] to yield 1.2 g of 2,7-*bis*[5-(4-hydroxyphenyl)thien-2-yl]-9,9-dipropylfluorene, Cr-I, 277 °C; N-I, 259 °C.

2.   **Preparation of 2-{4-[(*S*)-3,7-dimethyloct-6-enyloxy]phenyl}pyrimidine boronic acid.**

(a). A mixture of 4-bromophenol (34.6 g, 0.20 mol), (*S*)-(+)-citronelyl bromide (50g, 0.023 mol) and potassium carbonate (45 g, 0.33 mol) in butanone (500 cm^3) was heated under reflux overnight. The cooled reaction mixture was filtered and the filtrate concentrated under reduce pressure. The crude product was purified by fractional distillation to yield 42.3 g (68.2%) of 1-bromo-4-[(*S*)-3,7-dimethyloct-6-enyloxy]benzene.

(b). 2.5M *n*-Butylithium in hexanes (49.3 cm^3, 0.12 mol) was added dropwise to a cooled (-78 °C) solution of 1-bromo-4-[(*S*)-3,7-dimethyloct-6-enyloxy]benzene (35 g, 0.11 mol) in tetrahydrofuran (350 cm^3). The resultant solution was stirred at this temperature for 1 h and then trimethyl borate (23.8 g, 0.23 mol) was added dropwise to the mixture while maintaining the temperature at -78 °C. 20% hydrochloric acid (250 cm^3) was added and the resultant mixture was stirred for 1h and then extracted into diethyl ether (2 × 200 cm^3). The combined organic layers were washed with water (2 × 100 cm^3) and dried (MgSO$_4$). After filtration the solvent was removed under

26

reduce pressure to yield 20.35 g (65 %) of 4-[(S)-3,7-dimethyloct-6-enyloxy]phenyl boronic acid.

(c). A mixture of *tetrakis*(triphenylphosphine)palladium(0) (2 g, 1.73 x 10^{-3} mol), 5-bromo-2-iodopyrimidine (10 g, 3.5 x 10^{-2} mol), 4-(3,7-dimethyl-oct-6enyloxy)phenyl boronic acid (10.6 g, 3.85 x 10^{-2} mol), 20% sodium carbonate solution (50 cm^3) and 1,2-dimethoxyethane (150 cm^3). The reaction mixture was heated under reflux overnight. The cooled reaction mixture was extracted with dichloromethane (2 x 100 cm^3) and the combined organic layers were washed with brine (2 x 50 cm^3) and dried (MgSO4). After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane as the eluent followed by recrystallisation from ethanol to yield 7.5 g (55.1%) of 5-bromo-2-{4-[(S)-3,7-dimethyloct-6-enyloxy]phenyl}pyrimidine.

(d). 2.5*M* *n*-Butylithium in hexanes (8.72 cm^3, 2.18 x 10^{-2} mol) was added dropwise to a cooled (-78 °C) solution of bromo-2-{4-[(S)-3,7-dimethyloct-6-enyloxy] phenyl}pyrimidine (7 g, 1.81 x 10^{-2} mol) in tetrahydrofuran (150 cm^3). The resultant solution was stirred at this temperature for 1 h and then trimethyl borate (3.7 g, 3.59 x 10^{-2} mol) was added dropwise to the mixture while maintaining the temperature at -78 °C. On complete addition the mixture was allowed to warm to room temperature overnight. 20% hydrochloric acid (250 cm^3) was added and the resultant mixture stirred for 1 h and then extracted into dichloromethane (2 x 200 cm^3). The combined organic layers were washed with water (2 x 100 cm^3) and dried (MgSO4). After filtration the solvent was removed under reduce pressure to yield 4.2 g (65 %) of 2-{4-[(S)-3,7-dimethyloct-6-enyloxy] phenyl}pyrimidine boronic acid.

3.   **Preparation of 5-tributylestannyl-2-[(S)-3,7-dimethyloct-6-enyl]thiophene**

(a). 2.5*M* *n*-Butyllithium in hexanes (62.cm^3, 0.155 mol) was added slowly to a solution of thiophene (12.6 g, 0.15 mol) in tetrahydrofuran (150 cm^3) at -78°C. The

solution was stirred for 1 h at -78°C, (S)-(+)-citronelyl bromide (35 g, 0.16 mol) was added slowly and the temperature raised to RT after completion of the addition. 20% hydrochloric acid (100 cm³) and water (100 cm³) were added and the product extracted into diethyl ether (2 x 100 cm³). The organic extracts were dried (MgSO₄), filtered and evaporated down under partially reduced pressure. The crude product was purified by distillation to yield 17.6 g (54 %) of 2-[(S)-3,7-dimethyloct-6-enyl]thiophene.

(b). 2.5M n-Butyllithium in hexanes (41.2 cm³, 0.1 mol) was added slowly to a solution of 2-[(S)-3,7-dimethyloct-6-enyl]thiophene (17.6 g, 0.08 mol) in tetrahydrofuran (dry, 100 cm³) at -78°C. The solution was stirred for 1 h at -78°C, tri-n-butyltin chloride (39 g, 0.12 mol) was added slowly and the temperature allowed to rise to RT after completion of the addition. 20% Hydrochloric acid (100 cm³) and water (100 cm³) were added and the product extracted into diethyl ether (2x 100 cm³). The organic extracts were dried (MgSO₄) , filtered and evaporated down under partially reduced pressure. The crude product was purified by distillation to yield 21.0 g (51 %) of 5-tributylestannyl-2-[(S)-3,7-dimethyloct-6-enyl]thiophene.

4.   4,7-*bis*(5-bromothien-2-yl)-2,1,3-benzothiadiazole

(a). Bromine (52.8 g, 0.33mol) was added to a solution of 2,1,3-benzothiadiazole (8.1 g, 0.032 mol) in 47% hydrobromic acid (100 cm³) and the resultant solution heated under reflux for 2.5 h. The cooled reaction mixture was filtered and the solid residue washed with water (200 cm³) and sucked dry. The crude product was purified by recrystallisation from ethanol to yield 21.0 g (65 %) of 4,7-dibromo-2,1,3-benzothiadiazole.

(b). A mixture of 4,7-dibromo-2,1,3-benzothiadiazole (5.0 g, 0.016 mol), 2-(tributylstannyl)thiophene (15.7 g, 0.042 mol) and *tetrakis*(triphenylphosphine)palladium(0) (0.3 g, 2.6 × 10⁻⁴ mol) in N,N-dimethylformamide (50 cm³) was heated at 90 °C for 24 h. Dichloromethane (200

28

cm^3) was added to the cooled reaction mixture. The resultant solution was washed with 20% hydrochloric acid (2 x 150 cm^3) and water (100 cm^3), dried (MgSO$_4$) and then concentrated onto silica gel for purification by column chromatography [silica gel, dichloromethane: hexane 1:4]. The compound was further purified by recrystallisation from dichloromethane: ethanol to yield 3.8 g (79%) of 4,7-*bis*(5-bromothien-2-yl)-2,1,3-benzothiadiazole.

(c). *N*-Bromosuccinimide (3.73 g, 0.021 mol freshly purified by recrystallisation from water) was added slowly to a stirred solution of compound 4,7-*bis*(5-bromothien-2-yl)-2,1,3-benzothiadiazole (3 g, 0.01 mol) in chloroform (100 cm^3) and glacial acetic acid (100 cm^3). The solution was heated under reflux for 1 h, dichloromethane (100 cm^3) added, washed with water (100 cm^3), 20% hydrochloric acid (150 cm^3), saturated aqueous sodium sulphite solution (50 cm^3), and dried (MgSO$_4$). The solvent was removed under reduced pressure and the product purified by recrystallisation from toluene to yield 3.2 g (70 %) of 4,7-*bis*(5-bromothien-2-yl)-2,1,3-benzothiadiazole.

5.   **Preparation of 1-vinylallyl (*S*)-6-bromo-4-methylhexanoate**

(a). A solution of *m*-chloroperbenzoic acid (28.1 g) and dichloromethane (150 cm^3) was added dropwise to a cooled (ice bath) solution of (*S*)-(+)-citronellyl bromide (25.0 g) and dichloromethane (250 cm^3) at a rate sufficient to maintain the temperature below 10 °C. After the addition was complete, the mixture was stirred at 0 °C for 15 h. The reaction mixture was filtered to remove precipitated *m*-chlorobenzoic acid and the filtrate washed with an aqueous saturated sodium hydrogen sulphite solution (150 cm^3). The organic layer was separated off, dried (MgSO$_4$), filtered and then evaporated down under reduced pressure to yield 24.3 g, (90.3%) of 3-[(*S*)-5-bromo-3-methylpentyl]-2,2-dimethyloxirane.

(b). Periodic acid (12.1 g, 0.0590 mol) was added portion wise to a solution of 3-[(*S*)-5-bromo-3-methylpentyl]-2,2-dimethyloxirane (12.4 g, 0.0529 mol) in tetrahydrofuran (500 cm^3) at room temperature. After the addition was complete the reaction mixture

was stirred for 0.5 h and then poured onto water (500 cm^3). Most of the tetrahydrofuran was removed under reduced pressure and the resultant aqueous layer extracted with diethyl ether (3 x 500 cm^3). The combined organic layers were dried (MgSO$_4$), evaporated down under partially reduced pressure and the residue purified by column chromatography on silica gel[2] using a mixture of ethyl acetate/hexane (1:9) as eluent to yield 5.6 g (55.1%) of (S)-6-bromo-4-methylhexanal.

(c). Jones' reagent[3] was added dropwise to a solution of (S)-6-bromo-4-methylhexanal (5.0 g, 0.026 mol) in acetone (30 cm^3) at 0 °C at such a rate as to maintain the temperature of the solution below 10 °C. Upon completion of the oxidation propan-2-ol (12 cm^3) was added and the reaction mixture stirred at room temperature for 15 min., poured onto water (100 cm^3) and then extracted with diethyl ether (3 x 100 cm^3). The combined organic layers were washed with brine (2 x 100 cm^3), dried (MgSO$_4$) and then evaporated down under partially reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of ethyl acetate/hexane (1:9) as eluent to yield 3.8 g (69.3%) of (S)-6-bromo-4-methylhexanoic acid, which was used without further purification.

(d). A solution of N,N-dicyclohexylcarbodiimide (4.8 g, 0.023 mol) in dichloromethane (50 cm^3) was added to a solution of (S)-6-bromo-4-methylhexanoic acid (3.0 g, 0.023 mol), 1,4-pentadien-3-ol (1.7 g, 0.02 mol) and 4-(dimethylamino)pyridine (0.4 g) in dichloromethane (150 cm^3) at 0 °C. The reaction solution was stirred at room temperature overnight, filtered to remove precipitate and then evaporated down under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of dichloromethane/hexane (50:50) as eluent to yield 1-vinylallyl (S)-6-bromo-4-methylhexanoate.

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[2] The silica gel was pre-treated with a triethylamine/hexane (1:9) solution in order to prevent decomposition of the aldehyde during chromatography.
[3] [CrO$_3$ 1.5 g; concentrated H$_2$SO$_4$ 0.54 cm^3; H$_2$0, 9 cm^3.]

30

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